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GOLF BALL HAVING MULTI-LAYER COVER WITH UNIQUE OUTER COVER CHARACTERISTICS

Sub A1

Cross References to Related Applications

Sub A2

~~The present application is a continuation of U.S. Application Serial~~ No. 09/776,278 filed February 2, 2001 which is a continuation of U.S. Application Serial No. 09/470,196 filed on December 21, 1999, which is a continuation of U.S. application Serial No. 08/870,585 filed June 6, 1997, which is a continuation of U.S. Application Serial No. 08/556,237 filed November 9, 1995 now abandoned, which is a continuation-in-part of U.S. Application Serial No. 08/070,510 filed on ~~June 1, 1993, now abandoned~~.

Field of the Invention

The present invention relates to golf balls and, more particularly, to improved standard and oversized golf balls comprising multi-layer covers which have a comparatively hard inner layer and a relatively soft outer layer such as that produced by the use of a polyurethane based outer layer. The improved multi-layer golf balls provide for enhanced distance and durability properties over single layer cover golf balls while at the same time offering enhanced "feel" and spin characteristics generally associated with soft balata and balata-like covers of the prior art.

Background of the Invention

Traditional golf ball covers have been comprised of balata or blends of balata with elastomeric or plastic materials. The traditional balata covers are relatively soft and flexible. Upon impact, the soft balata covers compress against the surface of the club producing high spin. Consequently, the soft and flexible balata covers provide an experienced golfer with the ability to apply a spin to control the ball in flight in order to produce a draw or a fade, or a backspin which causes the ball to "bite" or stop abruptly on contact with the green. Moreover, the soft balata covers produce a soft "feel" to the low handicap player. Such

playability properties (workability, feel, etc.) are particularly important in short iron play with low swing speeds and are exploited significantly by relatively skilled players.

Despite all the benefits of balata, balata covered golf balls are easily cut and/or damaged if mis-hit. Golf balls produced with balata or balata-containing cover compositions therefore have a relatively short lifespan.

As a result of this negative property, balata and its synthetic substitutes, transpolyisoprene and transpolybutadiene, have been essentially replaced as the cover materials of choice by new cover materials comprising ionomeric resins.

Sub A3

~~Ionomeric resins are polymers containing interchain ionic bonding.~~ As a result of their toughness, durability and flight characteristics, various ionomeric resins sold by E. I. DuPont de Nemours & Company under the trademark Surlyn® and more recently, by the Exxon Corporation (see U. S. Patent No. 4,911,451) under the trademarks Escor® and Iotek®, have become the materials of choice for the construction of golf ball covers over the traditional "balata" (transpolyisoprene, natural or synthetic) rubbers. As stated, the softer balata covers, although exhibiting enhanced playability properties, lack the durability (cut and abrasion resistance, fatigue endurance, etc.) properties required ~~for repetitive play.~~

Ionomeric resins are generally ionic copolymers of an olefin, such as ethylene, and a metal salt of an unsaturated carboxylic acid, such as acrylic acid, methacrylic acid, or maleic acid. Metal ions, such as sodium or zinc, are used to neutralize some portion of the acidic group in the copolymer resulting in a thermoplastic elastomer exhibiting enhanced properties, i.e. durability, etc., for golf ball cover construction over balata. However, some of the advantages gained in increased durability have been offset to some degree by the decreases produced in playability. This is because although the ionomeric resins are very durable, they tend to be very hard when utilized for golf ball cover construction, and thus lack the degree of softness required to impart the spin necessary to control the ball in flight. Since the ionomeric resins are harder than balata, the ionomeric resin covers do not compress as much against the face of the club upon

impact, thereby producing less spin. In addition, the harder and more durable ionomeric resins lack the "feel" characteristic associated with the softer balata related covers.

As a result, there are currently more than fifty (50) commercial grades of ionomers available both from DuPont and Exxon, with a wide range of properties which vary according to the type and amount of metal cations, molecular weight, composition of the base resin (i.e., relative content of ethylene and methacrylic and/or acrylic acid groups) and additive ingredients such as reinforcement agents, etc. However, a great deal of research continues in order to develop a golf ball cover composition exhibiting not only the improved impact resistance and carrying distance properties produced by the "hard" ionomeric resins, but also the playability (i.e., "spin", "feel", etc.) characteristics previously associated with the "soft" balata covers, properties which are still desired by the more skilled golfer.

Consequently, a number of two-piece (a solid resilient center or core with a molded cover) and three-piece (a liquid or solid center, elastomeric winding about the center, and a molded cover) golf balls have been produced by the present inventor and others to address these needs. The different types of materials utilized to formulate the cores, covers, etc. of these balls dramatically alter the balls' overall characteristics.

Sub A4

In addition, ~~multi-layered covers containing one or more ionomer~~ resins have also been formulated in an attempt to produce a golf ball having the overall distance, playability and durability characteristics desired. For example, this was addressed by Spalding Sports Worldwide, Inc., the assignee of the present invention, in U. S. Patent No. 4,431,193 where a multi-layered, regular ~~sized, golf ball is disclosed.~~

In the '193 patent, a multi-layer golf ball is produced by initially molding a first cover layer on a spherical core and then adding a second layer. The first layer is comprised of a hard, high flexural modulus resinous material such as type 1605 Surlyn® (now designated Surlyn® 8940). Type 1605 Surlyn® (Surlyn® 8940) is a sodium ion based low acid (less than or equal to 15 weight percent methacrylic acid) ionomer resin having a flexural modulus of about 51,000 psi. An

outer layer of a comparatively soft, low flexural modulus resinous material such as type 1855 Surlyn® (now designated Surlyn® 9020) is molded over the inner cover layer. Type 1855 Surlyn® (Surlyn® 9020) is a zinc ion based low acid (10 weight percent methacrylic acid) ionomer resin having a flexural modulus of about 14,000 psi.

The '193 patent teaches that the hard, high flexural modulus resin which comprises the first layer provides for a gain in coefficient of restitution over the coefficient of restitution of the core. The increase in the coefficient of restitution provides a ball which serves to attain or approach the maximum initial velocity limit of 255 feet per second as provided by the United States Golf Association (U.S.G.A.) rules. The relatively soft, low flexural modulus outer layer provides essentially no gain in the coefficient of restitution but provides for the advantageous "feel" and playing characteristics of a balata covered golf ball.

Unfortunately, however, while a ball of the '193 patent does exhibit enhanced playability characteristics with improved distance (i.e. enhanced C.O.R. values) over a number of other then known multi-layered balls, the ball suffers from poor cut resistance and relatively short distance (i.e. lower C.O.R. values) when compared to two-piece, single cover layer balls commercially available today. These undesirable properties make the ball produced in accordance with the '193 patent unacceptable by today's standards.

The present invention is directed to new multi-layer golf ball compositions which provide for enhanced coefficient of restitution (i.e, enhanced resilience or carrying distance) and/or durability properties when compared to the multi-layer balls found in the prior art, as well as improved outer cover layer softness and durability. As such, the playability characteristics (i.e., "feel", "click", "spin", etc.) are not diminished.

These and other objects and features of the invention will be apparent from the following summary and description of the invention, the drawings and from the claims.

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Summary of the Invention

~~The present invention is directed to improved multi-layer golf ball~~ cover compositions and the resulting multi-layer golf balls produced using the

improved compositions. The present invention provides, in the first aspect, a golf ball comprising a core, an inner cover layer having particular characteristics, and an outer cover layer, also with certain features. The inner cover layer has a Shore D hardness of at least 60 and comprises a blend of two or more low acid ionomer resins, each containing no more than 16% by weight of an alpha, beta-unsaturated carboxylic acid. The outer cover layer has a Shore D hardness of from about 55 to about 59, a thickness of from about 0.01 to about 0.07 inches, and comprises a polyurethane material.

In another aspect, the present invention provides a golf ball comprising a core, and an inner cover layer and an outer cover layer. The inner cover layer has a Shore D hardness of at least 60, and comprises a blend of two or more low acid ionomers, each containing no more than 16% by weight of an alpha, beta-unsaturated carboxylic acid. The outer cover layer has a Shore D hardness of from about 60 to about 68, a thickness of from about 0.01 to about 0.07 inches, and comprises a polyurethane material.

In yet another aspect, the present invention provides a golf ball comprising a core, an inner cover layer disposed on the core, and an outer cover layer disposed about the inner cover layer. The inner cover layer has a Shore D hardness of about 60 or more, and comprises an ionomeric resin including no more than 16% by weight of an alpha, beta-unsaturated carboxylic acid having a modulus of from about 15,000 to about 70,000 psi. The outer cover layer has a Shore D hardness of from about 55 to about 68, a thickness from about 0.01 to ~~about 0.07 inches, and comprises a~~ polyurethane ~~material.~~

It has been found that multi-layer golf balls having inner and outer cover layers exhibit higher C.O.R. values and have greater travel distance in comparison with balls made from a single cover layer. In addition, it has been found that use of an inner cover layer constructed of a blend of low acid (i.e., 16 weight percent acid or less) ionomer resins produces softer compression and higher spin rates than inner cover layers constructed of high acid ionomer resins. This is compounded by the fact that the softer polyurethane outer layer adds to the desirable "feel" and high spin rate while maintaining respectable resiliency. The soft outer layer allows the cover to deform more during impact and increases the

area of contact between the club face and the cover, thereby imparting more spin on the ball. As a result, the soft polyurethane cover provides the ball with a balata-like feel and playability characteristics with improved distance and durability.

Consequently, the overall combination of the inner and outer cover layers made from blends of low acid ionomer resins and polyurethane results in a standard size or oversized golf ball having enhanced resilience (improved travel distance) and durability (i.e. cut resistance, etc.) characteristics while maintaining and in many instances, improving the balls playability properties.

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~~The combination of a low acid ionomer blend inner cover layer with~~ a soft, relatively low modulus ionomer, polyurethane based elastomer outer cover layer provides for overall coefficient of restitution (i.e., excellent resilience) while at the same time demonstrating improved compression and spin. The outer cover layer generally contributes to a more desirable feel and high spin, particularly at ~~lower swing speeds with highly lofted clubs such as half wedge shots~~.

Two principal properties involved in golf ball performance are resilience and hardness. Resilience is determined by the coefficient of restitution (C.O.R.), the constant "e" which is the ratio of the relative velocity of two elastic spheres after direct impact to that before impact. As a result, the coefficient of restitution ("e") can vary from 0 to 1, with 1 being equivalent to an elastic collision and 0 being equivalent to an inelastic collision.

Resilience (C.O.R.), along with additional factors such as club head speed, angle of trajectory and ball configuration (i.e., dimple pattern) generally determine the distance a ball will travel when hit. Since club head speed and the angle of trajectory are factors not easily controllable by a manufacturer, factors of concern among manufacturers are the coefficient of restitution (C.O.R.) and the surface configuration of the ball.

The coefficient of restitution (C.O.R.) in solid core balls is a function of the composition of the molded core and of the cover. In balls containing a wound core (i.e., balls comprising a liquid or solid center, elastic windings, and a cover), the coefficient of restitution is a function of not only the composition of the center and cover, but also the composition and tension of the elastomeric windings. Although both the core and the cover contribute to the coefficient of

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restitution, the present invention is directed to the enhanced coefficient of restitution (and thus travel distance) which is affected by the cover composition.

In this regard, the coefficient of restitution of a golf ball is generally measured by propelling a ball at a given speed against a hard surface and measuring the ball's incoming and outgoing velocity electronically. As mentioned above, the coefficient of restitution is the ratio of the outgoing velocity to the incoming velocity. The coefficient of restitution must be carefully controlled in all commercial golf balls in order for the ball to be within the specifications regulated by the United States Golf Association (U.S.G.A.). Along this line, the U.S.G.A. standards indicate that a "regulation" ball cannot have an initial velocity (i.e., the speed off the club) exceeding 255 feet per second. Since the coefficient of restitution of a ball is related to the ball's initial velocity, it is highly desirable to produce a ball having sufficiently high coefficient of restitution to closely approach the U.S.G.A. limit on initial velocity, while having an ample degree of softness (i.e., hardness) to produce enhanced playability (i.e., spin, etc.).

The hardness of the ball is the second principal property involved in the performance of a golf ball. The hardness of the ball can affect the playability of the ball on striking and the sound or "click" produced. Hardness is determined by the deformation (i.e., compression) of the ball under various load conditions applied across the ball's diameter (i.e., the lower the compression value, the harder the material). As indicated in U.S. Patent No. 4,674,751, softer covers permit the accomplished golfer to impart proper spin. This is because the softer covers deform on impact significantly more than balls having "harder" ionomeric resin covers. As a result, the better player is allowed to impart fade, draw or backspin to the ball thereby enhancing playability. Such properties may be determined by various spin rate tests such as the "nine iron" spin rate test described below in the Examples.

Accordingly, the present invention is directed to an improved multi-layer cover which produces, upon molding each layer around a core (preferably a solid core) to formulate a multi-layer cover, a golf ball exhibiting enhanced distance (i.e., resilience) without adversely affecting, and in many instances,

improving the ball's playability (hardness/softness) and/or durability (i.e., cut resistance, fatigue resistance, etc.) characteristics.

These and other objects and features of the invention will be apparent from the following detailed description.

Brief Description of the Drawings

FIG. 1 is a cross-sectional view of a golf ball embodying the invention illustrating a core 10 and a cover 12 consisting of an inner layer 14 and an outer layer 16 having dimples 18; and

FIG. 2 is a diametrical cross-sectional view of a golf ball of the invention having a core 10 and a cover 12 made of an inner layer 14 and an outer layer 16 having dimple 18.

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~~Detailed Description of the Preferred Embodiments~~

The present invention relates to improved multi-layer golf balls, particularly a golf ball comprising a multi-layered cover 12 over a solid core 10, and method for making same.

The multi-layered cover 12 comprises two layers: a first or inner layer or ply 14 and a second or outer layer or ply 16. The inner layer 14 is comprised of a low acid (i.e. 16 weight percent acid or less) ionomer blend. Preferably, the inner layer is comprised of a blend of two or more low acid (i.e. 16 weight percent acid or less) ionomer resins neutralized to various extents by different metal cations. The inner cover layer may or may not include a metal stearate (e.g., zinc stearate) or other metal fatty acid salt. The purpose of the metal stearate or other metal fatty acid salt is to lower the cost of production without affecting the overall performance of the finished golf ball.

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The low acid ionomers which may ~~be suitable for use~~ in formulating the inner layer compositions of the subject invention are ionic copolymers which are the metal, i.e., sodium, zinc, magnesium, etc., salts of the reaction product of an olefin having from about 2 to 8 carbon atoms and an unsaturated monocarboxylic acid having from about 3 to 8 carbon atoms. Preferably, the ionomeric resins are copolymers of ethylene and either acrylic or methacrylic acid.

In some circumstances, an additional comonomer such as an acrylate ester (i.e., iso- or n-butylacrylate, etc.) can also be included to produce a softer terpolymer. The carboxylic acid groups of the copolymer are partially neutralized (i.e., approximately 10-75%, preferably 30-70%) by the metal ions. Each of the low acid ionomer resins which may be included in the cover layer compositions of the invention contains 16% by weight or less of a carboxylic acid.

The inner layer compositions include the low acid ionomers such as those developed and sold by E. I. DuPont de Nemours & Company under the trademark Surlyn® and by Exxon Corporation under the trademarks Escor® or Iotek®, or blends thereof.

The low acid ionomeric resins available from Exxon under the designation Escor® and or Iotek®, are somewhat similar to the low acid ionomeric resins available under the Surlyn® trademark. However, since the Escor®/Iotek® ionomeric resins are sodium or zinc salts of poly(ethylene-acrylic acid) and the Surlyn® resins are zinc, sodium, magnesium, etc. salts of poly(ethylene-methacrylic acid), distinct differences in properties exist.

When utilized in the construction of the inner layer of a multi-layered golf ball, it has been found that the low acid ionomer blends extend the range of compression and spin rates beyond that previously obtainable. More preferably, it has been found that when two or more low acid ionomers, particularly blends of sodium and zinc high acid ionomers, are processed to produce the covers of multi-layered golf balls, (i.e., the inner cover layer herein) the resulting golf balls will travel further and at an enhanced spin rate than previously known multi-layered golf balls. Such an improvement is particularly noticeable in enlarged or oversized golf balls.

For example, the normal size, multi-layer golf ball taught in 4,650,193 does not incorporate blends of low acid ionomeric resins of the present invention in the inner cover layer. In addition, the multi-layered ball disclosed in the '193 patent suffers substantially in durability in comparison with the present invention.

Furthermore, as shown in the Examples, use of an inner layer formulated from blends of lower acid ionomers produces multi-layer golf balls

having enhanced compression and spin rates. These are the properties desired by the more skilled golfer.

With respect to the outer layer 16 of the multi-layered cover of the present invention, the outer cover layer is comparatively softer than the low acid ionomer blend based inner layer. The softness provides for the enhanced feel and playability characteristics typically associated with balata or balata-blend balls. The outer layer or ply, is comprised of a relatively soft, low modulus (about 1,000 psi to about 10,000 psi) and low acid (less than 16 weight percent acid) ionomer, ionomer blend or a non-ionomeric elastomer such as, but not limited to, a polyurethane, a polyester elastomer such as that marketed by DuPont under the trademark Hytrel®, a polyurethane sold by BASF under the designation Baytec® or a polyether amide such as that marketed by Elf Atochem S.A. under the trademark Pebax®. The outer layer is fairly thin (i.e. from about 0.010 to about 0.070 in thickness, more desirably 0.03 to 0.06 inches in thickness for a 1.680 inch ball and 0.04 to 0.07 inches in thickness for a 1.72 inch ball), but thick enough to achieve desired playability characteristics while minimizing expense.

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~~Preferably, the outer layer includes a blend of hard and soft (low acid) ionomer resins such as those described in U. S. Patent Nos. 4,884,814 and 5,120,791, both incorporated herein by reference. Specifically, a desirable material for use in molding the cover layer comprises a blend of a high modulus (hard), low acid, ionomer with a low modulus (soft) low acid, ionomer to form a base ionomer mixture. A high modulus ionomer herein is one which measures from about 15,000 to about 70,000 psi as measured in accordance with ASTM method D-790. The hardness may be defined as at least 50 on the Shore D scale as measured in accordance with ASTM method D-2240.~~

~~A low modulus ionomer suitable for use in the outer layer blend has a flexural modulus measuring from about 1,000 to about 10,000 psi, with a hardness of about 20 to about 40 on the Shore D scale.~~

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~~The hard ionomer resins utilized to produce the cover layer composition hard/soft blends include ionic copolymers which are the sodium, zinc, magnesium or lithium salts of the reaction product of an olefin having from 2 to 8 carbon atoms and an unsaturated monocarboxylic acid having from 3 to 8 carbon~~

~~atoms. The carboxylic acid groups of the copolymer may be totally or partially (i.e. approximately 15-75 percent) neutralized.~~

The hard ionomeric resins are likely copolymers of ethylene and either acrylic and/or methacrylic acid, with copolymers of ethylene and acrylic acid being the most preferred. Two or more types of hard ionomeric resins may be blended into the outer cover layer compositions in order to produce the desired properties of the resulting golf balls.

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As discussed earlier herein, the ~~hard ionomeric~~ resins introduced under the designation Escor® and sold under the designation Iotek® are somewhat similar to the hard ionomeric resins sold under the Surlyn® trademark. However, since the Iotek® ionomeric resins are sodium or zinc salts of poly(ethylene-acrylic acid) and the Surlyn® resins are zinc or sodium salts of poly(ethylene-methacrylic acid) some distinct differences in properties exist. As more specifically indicated in the data set forth below, the hard Iotek® resins (i.e., the acrylic acid based hard ionomer resins) are the more preferred hard resins for use in formulating the cover layer blends for use in the present invention. In addition, various blends of Iotek® and Surlyn® hard ionomeric resins, as well as other available ionomeric resins, may be utilized in the present invention in a similar manner.

Examples of commercially available hard ionomeric resins which may be used in the present invention in formulating the inner and outer cover blends include the hard sodium ionic copolymer sold under the trademark Surlyn® 8940 and the hard zinc ionic copolymer sold under the trademark Surlyn® 9910. Surlyn® 8940 is a copolymer of ethylene with methacrylic acid and about 15 weight percent acid which is about 29 percent neutralized with sodium ions. This resin has an average melt flow index of about 2.8 gm/10 min. Surlyn® 9910 is a copolymer of ethylene and methacrylic acid with about 15 weight percent acid which is about 58 percent neutralized with zinc ions. The average melt flow index of Surlyn® 9910 is about 0.7 gm/10 min. The typical properties of Surlyn® 9910 ~~and 8940 are set forth below in Table 1:~~

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~~TABLE 1~~

Typical Properties of Commercially Available Hard Surlyn® Resins Suitable for Use in the Cover Layers of the Present Invention

	ASTM D	8940	9910	8920	8528	9970	9730
Cation Type		Sodium	Zinc	Sodium	Sodium	Zinc	Zinc
Melt flow index, gms/10 min.	D-1238	2.8	0.7	0.9	1.3	14.0	1.6
Specific Gravity, g/cm^3	D-792	0.95	0.97	0.95	0.94	0.95	0.95
Hardness, Shore D	D-2240	66	64	66	60	62	63
Tensile Strength, (kpsi), MPa	D-638	(4.8) 33.1	(3.6) 24.8	(5.4) 37.2	(4.2) 29.0	(3.2) 22.0	(4.1) 28.0
Elongation, %	D-638	470	290	350	450	460	460
Flexural Modulus, (kpsi) MPa	D-790	(51) 350	(48) 330	(55) 380	(32) 220	(28) 190	(30) 210
Tensile Impact (23°C) KJ/m$_2$ (ft.-lbs./in^2)	D-1822S	1020 (485)	1020 (485)	865 (410)	1160 (550)	760 (360)	1240 (590)
Vicat Softening ~~Temperature, °C~~	~~D-1525~~	~~63~~	~~62~~	~~58~~	~~73~~	~~61~~	~~73~~

Examples of the more pertinent acrylic acid based hard ionomer resins suitable for use in the present inner and outer cover composition sold under the Iotek® trademark by the Exxon Corporation include Iotek® 4000, Iotek® 4010, Iotek® 8000, Iotek® 8020 and Iotek® 8030. The typical properties of these and other Iotek® hard ionomers suited for use in formulating the inner and outer layer cover composition are set forth below in Table 2:

Sub A13

~~TABLE 2~~

Typical Properties of Iotek® Ionomers

Resin Properties	ASTM Method	Units	4000	4010	8000	8020	8030
Cation type			zinc	zinc	sodium	sodium	sodium
Melt index	D-1238	g/10 min.	2.5	1.5	0.8	1.6	2.8
Density	D-1505	kg/m^3	963	963	954	960	960
Melting Point	D-3417	°C	90	90	90	87.5	87.5
Crystallization Point	D-3417	°C	62	64	56	53	55
Vicat Softening Point	D-1525	°C	62	63	61	64	67
% Weight Acrylic Acid			16		11		
% of Acid Groups cation neutralized			30		40		
Plaque Properties (3 mm thick, compression molded)	**ASTM Method**	**Units**	**4000**	**4010**	**8000**	**8020**	**8030**
Tensile at break	D-638	MPa	24	26	36	31.5	28
Yield point	D-638	MPa	none	none	21	21	23
Elongation at break	D-638	%	395	420	350	410	395
1% Secant modulus	D-638	MPa	160	160	300	350	390
Shore Hardness D	D-2240	--	55	55	61	58	59
Film Properties (50 micron film 2.2:1 Blow-up ratio)			**4000**	**4010**	**8000**	**8020**	**8030**
Tensile at Break MD	D-882	MPa	41	39	42	52	47.4
Tensile at Break TD	D-882	MPa	37	38	38	38	40.5
Yield point MD	D-882	MPa	15	17	17	23	21.6
Yield point TD	D-882	MPa	14	15	15	21	20.7
Elongation at Break MD	D-882	%	310	270	260	295	305
Elongation at Break TD	D-882	%	360	340	280	340	345
1% Secant modulus MD	D-882	MPa	210	215	390	380	380
1% Secant modulus TD	D-882	MPa	200	225	380	350	345
Dart Drop Impact	D-1709	g/micron	12.4	12.5	20.3		

Resin Properties Cation type	ASTM Method	Units	7010 zinc	7020 zinc	7030 zinc
Melt Index	D-1238	g/10 min.	0.8	1.5	2.5
Density	D-1505	kg/m^3	960	960	960
Melting Point	D-3417	°C	90	90	90
Vicat Softening Point	D-1525	°C	60	63	62.5

Plaque Properties (3 mm thick, compression molded)	ASTM Method	Units	7010	7020	7030
Tensile at break	D-638	MPa	38	38	38
Yield Point	D-638	MPa	none	none	none
Elongation at break	D-638	%	500	420	395
~~Shore Hardness D~~	~~D-2240~~	~~--~~	~~57~~	~~55~~	~~55~~

A14

~~Comparatively, soft ionomers may be used in formulating the~~ hard/soft blends of the inner and outer cover compositions. These ionomers include acrylic acid based soft ionomers. They are generally characterized as comprising sodium or zinc salts of a terpolymer of an olefin having from about 2 to 8 carbon atoms, acrylic acid, and an unsaturated monomer of the acrylate ester class having from 1 to 21 carbon atoms. The soft ionomer is preferably a zinc based ionomer made from an acrylic acid base polymer in an unsaturated monomer of the acrylate ester class. The soft (low modulus) ionomers have a hardness from about 20 to about 40 as measured on the Shore D scale and a flexural modulus from about 1,000 to about 10,000, as measured in accordance ~~with ASTM method D-790.~~.

Certain ethylene-acrylic acid based soft ionomer resins developed by the Exxon Corporation under the designation Iotek® 7520 (referred to experimentally by differences in neutralization and melt indexes as LDX 195, LDX 196, LDX 218 and LDX 219) may be combined with known hard ionomers such as those indicated above to produce the inner and outer cover layers. The combination produces higher C.O.R.s at equal or softer hardness, higher melt flow (which corresponds to improved, more efficient molding, i.e., fewer rejects) as well as significant cost savings versus the outer layer of multi-layer balls produced by

~~other known~~ hard-soft ionomer ~~blends as a result of the lower overall raw materials costs~~ and improved ~~yields.~~

While the exact chemical composition of the resins to be sold by Exxon under the designation Iotek® 7520 is considered by Exxon to be confidential and proprietary information, Exxon's experimental product data sheet lists the following physical properties of the ethylene acrylic acid zinc ionomer developed by Exxon:

TABLE 3

Physical Properties of Iotek® 7520

Property	ASTM Method	Units	Typical Value
Melt Index	D-1238	g/10 min.	2
Density	D-1505	kg/m^3	0.962
Cation			Zinc
Melting Point	D-3417	°C	66
Crystallization Point	D-3417	°C	49
Vicat Softening Point	D-1525	°C	42

Plaque Properties (2 mm thick Compression Molded Plaques)

Property	ASTM Method	Units	Typical Value
Tensile at Break	D-638	MPa	10
Yield Point	D-638	MPa	None
Elongation at Break	D-638	%	760
1% Secant Modulus	D-638	MPa	22
Shore D Hardness	D-2240		32
Flexural Modulus	D-790	MPa	26
Zwick Rebound	ISO 4862	%	52
De Mattia Flex Resistance	D-430	Cycles	>5000

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~~In addition, test data collected by the Assignee indicates that Iotek®~~ 7520 resins have Shore D hardnesses of about 32 to 36 (per ASTM D-2240), melt flow indexes of 3±0.5 g/10 min (at 190°C. per ASTM D-1288), and a flexural modulus of about 2500-3500 psi (per ASTM D-790). Furthermore, testing by an independent testing laboratory by pyrolysis mass spectrometry indicates that

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Iotek® 7520 resins are generally zinc salts of a terpolymer of ethylene, acrylic acid, and methyl acrylate.

Furthermore, it has been found that a grade of an acrylic acid based soft ionomer available from the Exxon Corporation under the designation Iotek® 7510, is also effective, when combined with the hard ionomers indicated above in producing golf ball covers exhibiting higher C.O.R. values at equal or softer hardness than those produced by known hard-soft ionomer blends. In this regard, Iotek® 7510 has the advantages (i.e. improved flow, higher C.O.R. values at equal hardness, increased clarity, etc.) produced by the Iotek® 7520 resin when compared to the methacrylic acid base soft ionomers known in the art (such as the Surlyn® 8625 and the Surlyn® 8629 combinations disclosed in U.S. Patent No. ~~4,884,814).~~

In addition, Iotek® 7510, when compared to Iotek® 7520, produces slightly higher C.O.R. valves at equal softness/hardness due to the Iotek® 7510's higher hardness and neutralization. Similarly, Iotek® 7510 produces better release properties (from the mold cavities) due to its slightly higher stiffness and lower flow rate than Iotek® 7520. This is important in production where the soft covered balls tend to have lower yields caused by sticking in the molds and subsequent punched pin marks from the knockouts.

According to Exxon, Iotek® 7510 is of similar chemical composition as Iotek® 7520 (i.e. a zinc salt of a terpolymer of ethylene, acrylic acid, and methyl acrylate) but is more highly neutralized. Based upon FTIR analysis, Iotek® 7520 is estimated to be about 30-40 wt.-% neutralized and Iotek® 7510 is estimated to be about 40-60 wt.-% neutralized. The typical properties of Iotek® 7510 in comparison of those of Iotek® 7520 are set forth below:

TO 180

TABLE 4

Physical Properties of Iotek® 7510
in Comparison to Iotek® 7520

	IOTEK® 7520	IOTEK® 7510
MI, g/10 min	2.0	0.8
Density, g/cc	0.96	0.97
Melting Point, °F	151	149
Vicat Softening Point, °F	108	109
Flex Modulus, psi	3800	5300
Tensile Strength, psi	1450	1750
Elongation, %	760	690
Hardness, Shore D	32	35

A33

It has been determined that when high acid/low acid ionomer blends are used for the cover layers, good results are achieved when the relative combination is in a range of about 90 to about 10 percent hard ionomer and about 10 to about 90 percent soft ionomer. The results are improved by adjusting the range to about 75 to 25 percent hard ionomer and 25 to 75 percent soft ionomer. Even better results are noted at relative ranges of about 60 to 90 percent hard ionomer resin and about 40 to 60 percent soft ionomer resin.

Specific formulations which may be used in the cover composition are included in the examples set forth in U. S. Patent No. 5,120,791 and 4,884,814. The present invention is in no way limited to those examples.

Moreover, in alternative embodiments, the outer cover layer formulation may also comprise a soft, low modulus non-ionomeric thermoplastic elastomer including a polyester polyurethane such as B.F.Goodrich Company's Estane® polyester polyurethane X-4517. According to B.F.Goodrich, Estane® X-4517 has the following properties:

Properties of Estane® X-4517

Tensile	1430
100%	815
200%	1024
300%	1193
Elongation	641
Youngs Modulus	1826

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Hardness A/D	88/39
Dayshore Rebound	59
Solubility in Water	Insoluble
Melt processing temperature	>350°F (>177°C)
Specific Gravity (H_2O=1)	1.1-1.3

Sub B1

~~Other soft, relatively low modulus non-ionomeric thermoplastic~~ elastomers may also be utilized to produce the outer cover layer as long as the non-ionomeric thermoplastic elastomers produce the playability and durability characteristics desired without adversely effecting the enhanced characteristics produced by the low acid ionomer resin composition. These include, but are not limited to thermoplastic polyurethanes such as: Texin® thermoplastic polyurethanes from Mobay Chemical Co. and the Pellethane® thermoplastic polyurethanes from Dow Chemical Co.; Ionomer/rubber blends such as those in Spalding U.S. Patents 4,986,545; 5,098,105 and 5,187,013; and, Hytrel® polyester ~~elastomers from DuPont and Pebax® polyetheramides from Elf Atochem S.A.~~

Similarly, a castable, thermosetting polyurethane produced by BASF under the trade designation Baytec® has also shown enhanced cover formulation properties. According to BASF, Baytec® (such as Baytec® RE 832), relates to a group of reactive elastomers having outstanding wear resistance, high mechanical strength, high elasticity and good resistance to weathering, moisture and chemicals. The Baytec® RE-832 system gives the following typical physical properties:

A34

Property	ASTM Test Method	Unit	Value
Tear Strength Die C	D624	psi	180
Stress at			
100% Modulus	D412	psi	320
200% Modulus			460
300% Modulus			600
Ultimate Strength	D412	psi	900
Elongation at Break	D412	%	490
Taber Abrasion	D460, H-18	mg/1000 cycles	350

TC/90

19

A34 cont

Component[1] Properties	Part A (Isocyanate)	Part B (Resin)
Viscosity @ 25°C, mPa·s	2500	2100
Density @ 25°C, g/cm	1.08	1.09
NCO, %	9.80	-----------
Hydroxyl Number, Mg KOH/g	------------	88

[1]Component A is a modified diphenylmethane diisocyanate (MDI) prepolymer and component B is a polyether polyol blend.

In preparing golf balls in accordance with the present invention, a hard inner cover layer is molded (by injection molding or by compression molding) about a core (preferably a solid core). A comparatively softer outer layer is molded over the inner layer.

The conventional solid core is about 1.545 inches in diameter, although it can range from about 1.495 to about 1.575 inches. Conventional solid cores are typically compression molded from a slug of uncured or lightly cured elastomer composition comprising a high cis content polybutadiene and a metal salt of an α, β, ethylenically unsaturated carboxylic acid such as zinc mono or diacrylate or methacrylate. To achieve higher coefficients of restitution in the core, the manufacturer may include fillers such as small amounts of a metal oxide such as zinc oxide. In addition, larger amounts of metal oxide than those that are needed to achieve the desired coefficient are often included in conventional cores in order to increase the core weight so that the finished ball more closely approaches the U.S.G.A. upper weight limit of 1.620 ounces. Other materials may be used in the core composition including compatible rubbers or ionomers, and low molecular weight fatty acids such as stearic acid. Free radical initiators such as peroxides are admixed with the core composition so that on the application of heat and pressure, a complex curing cross-linking reaction takes place.

The inner cover layer which is molded over the core is about 0.100 inches to about 0.010 inches in thickness, preferably about 0.0375 inches thick. The outer cover layer is about 0.010 inches to about 0.050 inches in thickness, preferably 0.0300 inches thick. Together, the core, the inner cover layer and the outer cover layer combine to form a ball having a diameter of 1.680 inches or

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more, the minimum diameter permitted by the rules of the United States Golf Association and weighing about 1.620 ounces.

Additional materials may be added to the cover compositions (both inner and outer cover layer) of the present invention including dyes (for example, Ultramarine Blue sold by Whitaker, Clark and Daniels of South Plainsfield, N.J.) (see U.S. Patent No. 4,679,795); pigments such as titanium dioxide, zinc oxide, barium sulfate and zinc sulfate; and UV absorbers; antioxidants; antistatic agents; and stabilizers. Further, the cover compositions of the present invention may also contain softening agents, such as plasticizers, processing aids, etc. and reinforcing material such as glass fibers and inorganic fillers, as long as the desired properties produced by the golf ball covers are not impaired.

Sub A6

~~The various cover composition layers of the present invention may~~ be produced according to conventional melt blending procedures. In the case of the outer cover layer, when a blend of hard and soft, low acid ionomer resins are utilized, the hard ionomer resins are blended with the soft ionomeric resins and with a masterbatch containing the desired additives in a Banbury mixer, two-roll mill, or extruder prior to molding. The blended composition is then formed into slabs and maintained in such a state until molding is desired. Alternatively, a simple dry blend of the pelletized or granulated resins and color masterbatch may be prepared and fed directly into the injection molding machine where homogenization occurs in the mixing section of the barrel prior to injection into the mold. If necessary, further additives such as an inorganic filler, etc., may be added and uniformly mixed before initiation of the molding process. A similar process is utilized to formulate the high acid ionomer resin compositions used to ~~produce the inner cover layer.~~

The golf balls of the present invention can be produced by molding processes currently well known in the golf ball art. Specifically, the golf balls can be produced by injection molding or compression molding the inner cover layer about wound or solid molded cores to produce an intermediate golf ball having a diameter of about 1.50 to 1.67 inches, preferably about 1.620 inches. The outer layer is subsequently molded over the inner layer to produce a golf ball having a diameter of 1.680 inches or more. Although either solid cores or wound cores can

be used in the present invention, as a result of their lower cost and superior performance, solid molded cores are preferred over wound cores.

In compression molding, the inner cover composition is formed via injection at about 380°F to about 450°F into smooth surfaced hemispherical shells which are then positioned around the core in a mold having the desired inner cover thickness and subjected to compression molding at 200° to 300°F for about 2 to 10 minutes, followed by cooling at 50°to 70°F for about 2 to 7 minutes to fuse the shells together to form a unitary intermediate ball. In addition, the intermediate balls may be produced by injection molding wherein the inner cover layer is injected directly around the core placed at the center of an intermediate ball mold for a period of time in a mold temperature of from 50°F to about 100°F. Subsequently, the outer cover layer is molded about the core and the inner layer by similar compression or injection molding techniques to form a dimpled golf ball of a diameter of 1.680 inches or more.

After molding, the golf balls produced may undergo various further processing steps such as buffing, painting and marking as disclosed in U.S. Patent No. 4,911,451.

Sub A17

~~The resulting golf ball produced from the low acid ionomer resin~~ inner layer and the relatively softer, low flexural modulus outer layer provide for an improved multi-layer golf ball which provides for desirable coefficient of restitution and durability properties while at the same time offering the feel and spin ~~characteristics associated with soft balata and balata-like covers of the prior art~~.

The present invention is further illustrated by the following examples in which the parts of the specific ingredients are by weight. It is to be understood that the present invention is not limited to the examples, and various changes and modifications may be made in the invention without departing from the spirit and scope thereof.

Example 1

Several intermediate balls (cores plus inner cover layers) were prepared in accordance with conventional molding procedures described above. The inner cover compositions were molded around 1.545 inch diameter cores

weighing 36.5 grams such that the inner cover had a wall thickness of about 0.0675 inches, with the overall ball measuring about 1.680 inches in diameter.

The cores utilized in the examples were comprised of the following ingredients: high cis-polybutadiene, zinc diacrylate, zinc oxide, zinc stearate, peroxide, calcium carbonate, etc. The molded cores exhibited Riehle compressions of about 60 and C.O.R. values of about .800. A representative formulation of the molded cores is set forth below:

MATERIAL	WEIGHT
BR-1220 (high cis-polybutadiene)	70.70
Taktene® 220 (high cis-polybutadiene)	29.30
React Rite™ ZDA (zinc diacrylate)	31.14
Zinc Oxide	6.23
Zinc Stearate	20.15
Limestone	17.58
Ground Flash (20-40 Mesh)	20.15
Blue Masterbatch	.012
Luperco® 231XL or Trigonox® 29/40	.89
Papi® 94	.50

[1]Blue Masterbatch consists of unknown compositions used only for internal identification purposes and has no effect on physical properties.

The inner cover compositions designated herein as compositions A-E utilized to formulate the intermediate balls are set forth in Table 7 below. The resulting molded intermediate balls were tested to determine the individual compression (Riehle), C.O.R., Shore C hardness, spin rate and cut resistance properties. These results are also set forth in Table 7 below.

The data of these examples are the average of twelve intermediate balls produced for each example. The properties were measured according to the following parameters:

Sub A8

~~Coefficient of restitution (C.O.R.) was measured by firing the~~ resulting golf ball in an air cannon at a velocity of 125 feet per second against a steel plate. The rebound velocity was then measured. The rebound velocity was divided by the forward velocity to give a coefficient of restitution. Details for this

~~procedure are set forth in U.S. Patent 5,984,806, herein incorporated by reference.~~

Shore hardness was measured generally in accordance with ASTM test 2240.

Cut resistance was measured in accordance with the following procedure: A golf ball is fired at 135 feet per second against the leading edge of a pitching wedge wherein the leading edge radius is 1/32 inch, the loft angle is 51 degrees, the sole radius is 2.5 inches and the bounce angle is 7 degrees.

The cut resistance of the balls tested herein was evaluated on a scale of 1 to 5. The number 1 represents a cut that extends completely through the cover to the core. A 2 represents a cut that does not extend completely through he cover but that does break the surface. A 3 does not break the surface of the cover but does leave a permanent dent. A 4 leaves only a slight crease which is permanent but not as severe as 3. A 5 represents virtually no visible indentation or damage of any sort.

The spin rate of the golf ball was measured by striking the resulting golf balls with a pitching wedge or 9 iron wherein the club head speed is about 105 feet per second and the ball is launched at an angle of 26 to 34 degrees with an initial velocity of about 110 to 115 feet per second. The spin rate was measured by observing the rotation of the ball in flight using stop action Strobe photography.

Initial velocity is the velocity of a ball when struck at a hammer speed of 143.8 feet per second in accordance with a test as prescribed by the U.S.G.A.

As will be noted, compositions A, B and C include high acid ionomeric resins (16% or more acid), with composition B further including zinc stearate. Composition D represents the inner layer (i.e. Surlyn® 1605) used in U.S. Patent No. 4,431,193. Composition E provides a hard, low acid ionomeric resin blend.

Sub A9

~~The purpose behind producing and testing the balls of Table 11 was to provide a subsequent comparison in properties with the multi-layer golf balls of the present invention.~~

Table 5

Molded Intermediate Golf Balls

Ingredients of Inner Cover Compositions	A	B	C	D	E
Iotek® 959	50	50	--	--	--
Iotek® 960	50	50	--	--	--
Zinc Stearate	--	50	--	--	--
Surlyn® 8162	--	--	75	--	--
Surlyn® 8422	--	--	25	--	--
Surlyn® 1605	--	--	--	100	--
Iotek® 7030	--	--	--	--	50
Iotek® 8000	--	--	--	--	50
Properties of Molded Intermediate Balls					
Compression	58	58	60	63	62
C.O.R.	.811	.810	.807	.793	.801
Shore C Hardness	98	98	97	96	96
Spin Rate (R.P.M.)	7,367	6,250	7,903	8,337	7,956
Cut Resistance	4-5	4-5	4-5	4-5	4-5

As shown in Table 5 above, the high acid ionomer resin inner cover layer (molded intermediate balls A-C) have lower spin rates and exhibit higher resiliency characteristics than the low acid ionomer resin based inner cover layers of balls D and E.

Multi-layer balls in accordance with the present invention were then prepared. Specifically, the inner cover compositions used to produce intermediate golf balls from Table 5 were molded over the solid cores to a thickness of about 0.0375 inches, thus forming the inner layer. The diameter of the solid core with the inner layer measured about 1.620 inches. Alternatively, the intermediate golf balls of Table 5 were ground down using a centerless grinding machine to a size of 1.620 inches in diameter to produce an inner cover layer of 0.0375 inches.

The size of 1.620 inches was determined after attempting to mold the outer cover layer to various sizes (1.600", 1.610", 1.620", 1.630" and 1.640") of intermediate (core plus inner layer) balls. It was determined that 1.620" was about the largest "intermediate" ball (i.e., core plus inner layer) which could be easily molded over with the soft outer layer materials of choice. The goal herein was to use as thin an outer layer as necessary to achieve the desired playability characteristics while minimizing the cost of the more expensive outer materials.

25

However, with a larger diameter final golf ball and/or if the cover is compression molded, a thinner cover becomes feasible.

Sub A20

~~With the above in mind, an outer cover layer composition was~~ blended together in accordance with conventional blending techniques. The outer layer composition used for this portion of the example is a relatively soft cover composition such as those listed in U.S. Patent No. 5,120,791. An example of such a soft cover composition is a 45% soft/55% hard low acid ionomer blend designated by the inventor as "TE-90". The composition of TE-90 is set forth below in Table 12 as follows:

<u>Outer Cover Layer Composition TE-90</u>

Iotek® 8000	22.7 weight %
Iotek® 7030	22.7 weight %
Iotek® 7520	45.0 weight %
White MB[1]	9.6 weight %

[1]White MB consists of about 23.77 weight percent TiO_2, 0.22 weight percent Uvitex® OB, 0.03 weight percent Santonox® R, 0.05 weight percent Ultramarine ~~Blue™ and 75.85 weight percent Iotek® 7030.~~

The above outer layer composition was molded around each of the 1.620 diameter intermediate balls comprising a core plus one of compositions A-D, respectively. In addition, for comparison purposes, Surlyn® 1855 (new Surlyn® 9020), the cover composition of the '193 patent, was molded about the inner layer of composition D (the intermediate ball representative of the '193 patent). The outer layer TE-90 was molded to a thickness of approximately 0.030 inches to produce a golf ball of approximately 1.680 inches in diameter. The resulting balls (a dozen balls for each example) were tested and the various properties thereof are set forth in Table 6A as follows:

TABLE 6A

Finished Balls

Ingredients:	1	2	3	4	5
Inner Cover Composition	A	B	C	D	D
Outer Cover Composition	TE-90	TE-90	TE-90	TE-90	Surlyn® 9020
Properties of Molded Finished Balls:					
Compression	63	63	69	70	61
C.O.R.	.784	.778	.780	.770	.757
Shore C Hardness	88	88	88	88	89
Spin (R.P.M.)	8,825	8,854	8,814	8,990	8,846
Cut Resistance	3-4	3-4	3-4	3-4	1-2

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SWB A21

~~As it will be noted in finished balls 1-4, by creating a multi-layer~~ cover utilizing the high acid ionomer resins in the inner cover layer and the hard/soft low acid ionomer resin in the outer cover layer, generally higher compression and increased spin rates are noted over the single layer covers of Table 11. In addition, both the C.O.R. and the Shore C hardness are reduced over the respective single layer covers of Table 11. This was once again particularly true with respect to the multi-layered balls containing the high acid ionomer resin in the inner layer (i.e. finished balls 1-4). In addition, with the exception of prior art ball 5 (i.e. the '193 patent), resistance to cutting remains good but is slightly decreased. As noted above, the prior art ball of the '193 patent suffers substantially in durability (as well as in resiliency) in comparison to the balls of the ~~present invention.~~

Furthermore, it is also noted that the use of the high acid ionomer resins as the inner cover material produces a substantial increase in the finished balls' overall distance properties. In this regard, the high acid ionomer resin inner covers of balls 1-3 produce an increase of approximately 10 points in C.O.R. over the low acid ionomer resin inner covers of balls 4 and about a 25 point increase over the prior art balls 5. Since an increase in 3 to 6 points in C.O.R. results in an

average increase of about 1 yard in distance, such an improvement is deemed to be significant.

Several other outer layer formulations were prepared and tested by molding them around the core and inner cover layer combination to form balls each having a diameter of about 1.68 inches. First, B.F.Goodrich Estane® X-4517 polyester polyurethane was molded about the core molded with inner layer cover formulation A. DuPont Surlyn® 9020 was molded about the core which was already molded with inner layer D. Similar properties tests were conducted on these golf balls and the results are set forth in Table 6B below:

~~TABLE 6B~~

Finished Balls

Ingredients:	6	7
Inner Cover Layer Composition	A	D
Outer Cover Layer Composition	Estane® 4517	Surlyn® 9020
Properties of Molded Finished Balls:		
Compression	67	61
C.O.R.	.774	.757
Shore C Hardness	74	89
Spin (R.P.M.)	10,061	8,846
Cut Resistance	3-4	1-2

The ball comprising inner layer formulation D and Surlyn® 9020 identifies the ball in the Nesbitt 4,431,193 patent. As is noted, the example provides for relatively high softness and spin rate though it suffers from poor cut resistance and low C.O.R. This ball is unacceptable by today's standards.

As for the Estane® X-4517 polyester polyurethane, a significant increase in spin rate over the TE-90 cover is noted along with an increased compression. However, the C.O.R. and Shore C values are reduced, while the cut resistance remains the same. Furthermore, both the Estane® X-4517 polyester polyurethane and the Surlyn® 9020 were relatively difficult to mold in such thin sections.

Example 2

In order to analyze the change in characteristics produced by multi-layer golf balls (standard size) having inner cover layers comprised of ionomer resin blends of different acid levels, a series of experiments were run. Specifically, 14 tests were performed, varying the type of core, inner cover layer and outer cover layer. The results are shown below:

TABLE 7

Sample #	Core	INNER LAYER	THICKNESS	COMP/ COR	OUTER COVER	THICKNESS	COMP (Rhiele)	COR	SHORE D	SPIN
8	1042 YELLOW	NONE	_____	SEE BELOW	TOP GRADE	0.055	61	.800	68	7331
9	1042 YELLOW	NONE	---------	SEE BELOW	959/960	0.055"	56	.808	73	6516
10	SPECIAL 1.47"	959/960	0/050"	65/.805	959/960	O.055"	48	.830	73	6258
11	1042 YELLOW	NONE	---------	SEE BELOW	SD 90	0.055"	62	.792	63	8421
12	SPECIAL 1.47"	TOP GRADE	0.050"	66/.799	SD 90	0.055"	55	.811	63	8265
13	SPECIAL 1.47"	959/960	0.050"	65/.805	SD 90	0.055"	53	.813	63	8254
14	SPECIAL 1.47"	TOP GRADE	0.050"	66/.799	TOP GRADE	0.055"	51	.819	68	7390
15	1042 YELLOW	NONE	---------	SEE BELOW	Z-BALATA	0.055"	67	.782	55	9479
16	SPECIAL 1.47"	959/960	0.050"	65/.805	Z-BALATA	0.055"	61	.800	55	9026
17	SPECIAL 1.47"	TOP GRADE	0.050"	66/.799	Z-BALATA	0.055"	60	.798	55	9262

1042 YELLOW>COMP=72, COR=.780
SPECIAL 1.47" CORE>COMP=67, COR=.782

Sub A23

~~In this regard, Top Grade or TG is a low acid inner cover ionomer~~ resin blend comprising of 70.6% Iotek® 8000, 19.9% Iotek® 7010 and 9.6% white masterbatch. "959/960" is a 50/50 wt/wt blend of Iotek® 959/960. In this regard, Escor® or Iotek® 959 is a sodium ion neutralized ethylene-acrylic neutralized ethylene-acrylic acid copolymer. According to Exxon, Iotek® 959 and 960 contain from about 19.0 to about 21.0% by weight acrylic acid with approximately 30 to about 70 percent of the acid groups neutralized with sodium and zinc ions, respectively. The physical properties of these high acid acrylic acid based ~~ionomers are as follows:~~

PROPERTY	ESCOR® (IOTEK®) 959	ESCOR® (IOTEK®) 960
Melt Index, g/10 min	2.0	1.8
Cation	Sodium	Zinc
Melting Point, °F	172	174
Vicat Softening Point, °F	130	131
Tensile @ Break, psi	4600	3500
Elongation @ Break, %	325	430
Hardness, Shore D	66	57
Flexural Modulus, psi	66,000	27,000

Furthermore, the low acid ionomer formulation for SD 90 and Z-Balata are set forth below:

SD Cover	ZB Cover
17.2% Surlyn® 8320	19% Iotek® 8000
7.5% Surlyn® 8120	19% Iotek® 7030
49% Surlyn® 9910	52.5% Iotek® 7520
16.4% Surlyn® 8940	9.5% white MB
9.7% white MB	

Sub A24

~~The data clearly indicates that higher C.O.R. and hence increased~~ travel distance can be obtained by using multi-layered covered balls versus balls covered with single layers. However, some sacrifices in compression and spin are also noted. Further, as shown in comparing Example Nos. 12 vs. 13, Example

Nos. 17 vs. 16, etc., use of lower acid level inner cover layers and relatively soft outer cover layers (i.e., 50 wt. % or more soft ionomer) produces softer compression and higher spin rates than the golf balls comprised of high acid inner cover layers. Consequently, use of blends of low acid ionomer resins to produce the inner layer of a multi-layer covered golf ball produces not only enhanced travel di~~stance but also enhanced compression and spin properties.~~

Example 3

Multi-layer oversized golf balls were produced utilizing different ionomer resin blends as the inner cover layer (i.e., core plus inner cover layer is defined as "mantel"). The "ball data" of the oversized multi-layer golf balls in comparison with production samples of Top-Flite® XL and Top-Flite® Z-Balata is set forth below.

TABLE 8

	18	19	20	21 Top-Flite® XL	22 Top-Flite® Z-Balata 90
Core Data					
Size	1.43	1.43	1.43	1.545	1.545
COR	.787	.787	.787	----	----
Mantle Data					
Material	TG	TG	TG	----	----
Size	1.61	1.61	1.61	----	----
Thickness	.090	.090	.090	----	----
Shore D	68	68	68	----	----
Compression	57	57	57	----	----
COR	.815	.815	.815	----	----
Ball Data					
Cover	TG	ZB	SD	TG	ZB
Size	1.725	1.723	1.726	1.681	1.683
Weight	45.2	45.1	45.2	45.3	45.5
Shore D	68	56	63	68	56
Compression	45	55	49	53	77
COR	.820	.800	.810	.809	.797
Spin	7230	9268	8397	7133	9287

The results indicate that use of multi-layer covers enhances C.O.R. and travel distance. Further, the data shows that use of a blend of low acid ionomer resins (i.e., Top Grade) to form the inner cover layer in combination with a soft outer cover (ZB or SD) produces enhanced spin and compression characteristics. The overall combination results in a relatively optimal golf ball with respect to characteristics of travel distances, spin and durability.

Example 4

Castable Polyurethane Covered Multi-layer Balls

A limited number of samples were made using BASF Baytec® RE232 polyurethane as a cover material over four different types of mantle cores. Controls included Z-Balata 100s along with the same mantle cores used for the polyurethane samples covered with Z-Balata cover stock. Mantle cores were made up of 82 and 58 compression cores covered with Iotek® 8030/7030.

Castable PU Molding Process

Materials used:

Baytec® RE832, mix ratio 9 parts A/12 parts B
1 - 1.57" i.d. smooth cavity
2 - 1.68" i.d. dimpled cavities
1 - 2" hose clamp
1 - bench vise or large C-clamp

Sub A25

~~(The smooth and dimpled cavities are the same O.D.)~~

The mantle core is 1.57" and fits snugly in the 1.57" cavity. The hose clamp is attached to the 1.57" cavity and a mantle core is placed inside. Urethane is mixed and poured into one of the dimpled cavities and the two halves are placed together and clamped, forcing out excess material and forming half the cover. The hose clamp is used to keep the two mold halves aligned during curing. When the cover material is set up enough (about 5 minutes), the two halves are separated and the 1.57" mold is replaced with the other 1.68" mold and the process is repeated. Both halves of the cover are now cast and the entire assembly is placed ~~in an 125°F oven for 1 hour after which it can be opened and the ball removed~~.

All samples were finished using normal production equipment and procedures. The properties of the finished balls are set forth below:

TABLE 9

	23	24	25	26	27	28	29	30
Core Data								
Size	1.47"	1.47"	1.47"	1.47"	1.47	1.47"	1.47"	1.47"
Weight	32.2	32	32.2	32	37.7	32.2	32	32.2
Comp	82	58	82	58	85	82	58	82
COR	768	772	768	772	794	768	772	768
Mantle Data	Iotek®	Iotek®	Iotek®	Iotek®		Iotek®	Iotek®	Iotek®
Material	8030/7030	8030/7030	8030/7030	8030/7030	None	8030/7030	8030/7030	8030/7030
Weight	37.8	38.1	37.9	38.1		37.8	38.1	37.9
Size	1.57"	1.57"	1.57"	1.57"		1.57"	1.57"	1.57"
Comp	70	48	69	48		70	48	69
COR	781	785	786	788		781	785	786
Ball Data								
Cover Material	Baytec® RE832	Baytec® RE832	Baytec® RE832	Baytec® RE832	Z-Balata	Z-Balata	Z-Balata	Z-Balata
Weight	45.4	45.5	45.5	45.2	45.3	44.8	45	
Comp	75	64	73	60	80	66	50	65
COR	771	763	770	761	792	775	774	778
Shore C	65	65	65	65	84	84	84	84
Spin (rpm)	9560	8789	9285	8760	8796	8702	9072	8643
Cut (1-good, 4-poor)	2	2	2	1.5	2	2	2	2
Scuff (1-good, 4-poor)	1.5	1.5	1.5	1.5	2	3	3	3

Table 9 contains the construction details and test results. Multilayer balls with the thermoset urethane covers (Examples 23-25) were softer in compression and similar in COR to the multi-layer balls with the Z-Balata cover (Examples 27-29). Shore C was much lower for the urethane balls and they were more resistant to scuff than any of the Z-Balata covered balls. Guillotine cut resistance was about the same. Spin rate comparison shows that the urethane samples are better than the Z-Balata covered balls.

Test results indicate that a very good multi-layer ball can be made using castable polyurethane cover material. Further, advantages include the molding of very thin covers, molding over very soft compression core/mantle, and low cost tooling.

Sub A2

The invention ~~has been described with reference to the preferred~~ embodiments. Obviously, modifications and alterations will occur to others upon reading and understanding the preceding detailed description. It is intended that the invention be construed as including all such modifications and alterations insofar as they come within the scope of the appended claims or the equivalents ~~thereof~~.